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Primary Standards and Standard Reference Materials for Electrolytic Conductivity

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Changes to the Special Publication

Table 2 (page 9)

The values reported in Table 2 for the 0.01 D and 0.1 D were based on the 1968 temperature scale (IPTS 1968). The values were corrected to the current temperature scale, IPTS 90, in Ref [11]. Additionally, the values of conductivity for 0.1 D KCl are low by a factor of 10.

The correct values using IPTS 90 are reported in the table below.

Table 2. Electrolytic Conductivity Values for 0.01D, 0.1D, and 1.0 D
KCl Solutions* and Water, ITS-90 Scale

$t/°C$	$10^4 \, \kappa / \, (\mu S/cm)$			
	0.01 D KCl[11]	0.1 D KCl[11]	1.0 D KCl[8]	H_2O[11]
0	773.09	7134.6	65 135	0.58
5	891.20	8200.0	73 860	0.68
10	1 014.2	9308.7	82 871	0.79
15	1 141.8	10 457	92 136	0.89
18	1 220.3	11 162	97 804	0.95
20	1 273.4	11 639	101 620	0.99
25	1 408.6	12 852	111 300	1.10
30	1 547.0	14 091	121 110	1.20
35	1 688.2	15 352	131 050	1.30
40	1 831.8	16 631	141 080	1.40
45	1 977.3	17 922	151 150	1.51
50	1 124.2	19 222	161 240	1.61

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Abstract

This report describes the principles and methods for measuring the electrolytic conductivity of primary standards and NIST Standard Reference Materials (SRMs). There are two methods for measuring conductivity: the direct current (DC) method, and the alternating current (AC) method. NIST has redetermined the conductivity of the primary standards, and determined a set of molality-based primary standards over a temperature range of 0 °C to 50 °C. The conductivities of the primary standards were determined using two uniquely designed conductivity cells for measuring resistance with the AC and DC methods. The primary standards are used to determine the cell constants of conductivity cells. In our laboratory, we used both Jones and Daggett cells for measuring conductivity. NIST issues a set of Standard Reference Materials (SRMs) available in nominal conductivity values of 5 µS/cm, 15 µS/cm, 25 µS/cm, 100 µS/cm, 500 µS/cm, 1 000 µS/cm, 10 000 µS/cm, 20 000 µS/cm, and 100 000 µS/cm. The certified conductivity values for the SRMs include the solvent conductivity.

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Glossary

A	constant for an electrolyte solution based on Kohlrausch's Square Root Law
A	effective cross-sectional area
c	concentration, units are specified as either mol/L, equivalents/L, or mol/kg
E_T	potential between the potential electrodes in the DC conductance cell
E_s	potential drop across the standard resistor in DC measurement
ΔE	average potential difference between two center Ag, AgCl electrodes in DC cell
F	force under which an ion moves
I	current
I	ionic strength (Section 1.2 only)
K_{cell}	cell constant of a conductivity cell
$K_{cell, T}$	cell constant of the center tube of either an AC or DC absolute conductivity cell
$K_{cell, W}$	cell constant of AC absolute conductivity cell with center tube
$K_{cell, N}$	cell constant of AC absolute conductivity cell without center tube
l	effective length between electrodes
q	mobility function (Eq. 9)
R	resistance
R_N	resistance of a solution in the AC absolute conductivity cell without center tube
R_s	resistance of standard resistor used in the DC absolute measurement
R_T	resistance of a solution in the center tube of the DC absolute conductivity cell
R_w	resistance of a solution in the AC absolute conductivity cell with center tube
r	radius of a sphere as defined by Stokes' Law
T	absolute temperature

t	temperature, °C
u	mobility of an ion
v	velocity of a sphere as defined by Stokes' Law
z	valence of an ion
z_1	valence of a cation
z_2	valence of an anion
ε	dielectric constant
η	viscosity of a homogenous medium
κ	electrolytic conductivity of an electrolyte solution
κ_{BA}	electrolytic conductivity of benzoic acid
κ_{KCl}	electrolytic conductivity of potassium chloride
Λ	equivalent conductivity of an electrolyte
Λ^o	equivalent conductivity of an electrolyte at infinite dilution
λ	ionic equivalent conductivity
λ^o	ionic equivalent conductivity at infinite dilution
λ_1^o	ionic equivalent conductivity at infinite dilution of a cation
λ_2^o	ionic equivalent conductivity at infinite dilution of an anion
ρ	resistivity
ω	frequency

1. Introduction

Electrolytic conductivity is the measure of a solution's ability to conduct current. The magnitude of the conductivity is dependent on the nature of the ions (i.e., charge, size and mobility) and the nature of the solvent (such as dielectric constant and viscosity). The electrolytic conductivity is a result of ionic movement in a particular solvent, which is related to the ionic interactions taking place within the solution. The measurement of electrolytic conductivity is a nonspecific measurement; all ions contribute to the electrolytic conductivity of the solution.

In order to have uniform conductivity measurements, accurate electrolytic conductivity standards must be available for industrial use. For this purpose, the National Institute of Standards and Technology (NIST) has developed a series of electrolytic conductivity Standard Reference Materials (SRMs) and issues them through its Standard Reference Materials Program. This report describes the theory and practice for preparing SRMs.

1.1 Principles of the Electrolytic Conductivity Measurement

The measurement of a solution's resistance, R, in a conductivity cell, is used to determine the conductivity of a solution. The resistance of a solution is proportional to the distance between the electrodes, l, and inversely proportional to the effective cross-sectional area, A:

$$R = \rho \frac{l}{A} \text{ , ohm} \tag{1}$$

The resistivity, ρ, is a constant for a given solution and is expressed in units of ohm·cm. Conductivity is defined as the reciprocal of resistivity:

$$\kappa = \frac{1}{\rho} = \frac{1}{R} \frac{l}{A} \text{ , ohm}^{-1} \text{ cm}^{-1} \text{ or S cm}^{-1} \tag{2}$$

The cell in which the conductivity is measured has a cell constant, K_{cell}, which is defined as

$$K_{cell} = \frac{l}{A} \ , \mathrm{cm}^{-1} \tag{3}$$

where l is the effective length between the electrodes and A is the effective cross sectional area. A useful definition for the electrolytic conductivity, κ, is obtained by combining Eq. (1-3),

$$\kappa = \frac{K_{cell}}{R} \ , \mathrm{S \ cm}^{-1} \tag{4}$$

where R is the resistance of the solution and K_{cell} is the cell constant.

Generally, a cell can be constructed in any shape; however, the cell volume and the positions of the electrodes must be rigidly fixed and, therefore, the effective physical dimensions of a cell, the l and A, are constant. The cell constant is determined by measuring the geometrical dimensions of the cell or by comparing with primary standard solutions in the cell. In the first case, l and A are measured directly. In the second case, the cell constant is determined from Eq. (4) with known κ and R. To determine the absolute standards, Kohlrausch measured the cell constant mechanically [1-3]. Jones and Bradshaw [4] used mercury, which then defined the international ohm, to determine their cell constants. Both of these measurements have been reviewed and the primary standards for determination of the cell constant were recommended [5].

NIST reconfirmed the old set of standards [6] and established a new set of primary standards. The new primary standards are based on the molality scale. The conductivity value for each standard has been determined at a wider range of temperatures than formerly available. In the following sections, a detailed description of these measurements will be given and discussed.

1.2 Equivalent Conductivity

Often, referring to equivalent conductivity, Λ, of a solution as opposed to electrolytic conductivity is desirable. The equivalent conductivity is related to the solution's ionic concentration.

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$$\Lambda = \frac{1000\kappa}{c} \, , \mathrm{S \, cm^2 \, equiv^{-1}} \tag{5}$$

where c is the concentration of the electrolyte expressed in equivalents per liter. The International Union of Pure and Applied Chemistry (IUPAC) has recommended that molar conductivity be used in place of equivalent conductivity. However, the electrolytic conductivity theory was developed in terms of equivalent conductivity and much of the data in the early work was reported in terms of equivalent conductivity. The old usage has been retained here to avoid confusion.

The equivalent conductivity, Λ, is the sum of the individual ionic conductivities, λ,

$$\Lambda = \lambda_1 + \lambda_2 + ... + \lambda_n \tag{6}$$

where the equivalent conductivity has units of $\mathrm{cm^2\Omega^{-1}equiv^{-1}}$. Similarly, the equivalent conductivity at infinite dilution, Λ°, is the sum of the individual ionic conductivities at infinite dilution, λ°. Kohlrausch's Law of Independent Migration of Ions states that when ions are far enough apart that the movement of one ion is not influenced by other ions present in solution, the ions are at infinite dilution [7].

Conductivity is dependent on the concentration of the electrolyte in solution. The equivalent conductivity of a strong electrolyte generally increases with increasing concentration due to an increase in the number of ions present. For strong electrolytes in dilute solution, the equivalent conductivity may be expressed emperically by the Kohlrausch Square Root Law [7]:

$$\Lambda = \Lambda^o - \mathrm{A}\sqrt{c} \tag{7}$$

where A is an empirical constant for a given electrolyte. Later, Onsager [8] used Debye-Hückel's

ionic theory to develop a limiting law for equivalent conductivity with the same form as Eq. 7, but

with a theoretical value for the constant A

$$A = \left[\frac{2801000|z_1 z_2| q \Lambda^o}{(\varepsilon T)^{\frac{3}{2}} (1 + \sqrt{q})} + \frac{41.25(|z_1| + |z_2|)}{\eta (\varepsilon T^{\frac{1}{2}})} \right] \sqrt{I} \tag{8}$$

where

$$q = \frac{|z_1 z_2|}{|z_1| + |z_2|} \times \frac{\lambda_1^o + \lambda_2^o}{|z_2| \lambda_1^o + |z_1| \lambda_2^o} \tag{9}$$

and z_1 is the valency of the cation, z_2 is the valency of the anion, ε is the dielectric constant, η is the

viscosity, T is the absolute temperature, and I is the ionic strength.

1.3 Electrolytic Conductivity of Water

The electrolytic conductivity of an electrolyte solution consists of the conductivity of the

solvent and the conductivity of the solute. Hence, the conductivity of water (typically the solvent) is

important. The equivalent conductivity, Λ, of pure water at 25 °C is 0.055 μS cm^{2}equiv^{-1}[9].

Equation (5) can be used to calculate the theoretical electrolytic conductivity of water. For

water at 25 °C, the pK_w = 14 and therefore, the concentration of H$^+$ and OH$^-$ ions from dissociated

water molecules is $c_{H+} = c_{OH-} = 10^{-7}$ equivalents per liter. The λ^o for H$^+$ is 349.81 S cm^2 equiv^{-1} and

the λ^o for OH$^-$ is 198.3 S cm^2 equiv^{-1} [7]. The electrolytic conductivity of water is calculated by

$$\Lambda^o_{water} = \lambda^o_{H^+} + \lambda^o_{OH^-} = [198.3 + 349.81] \, S \, cm^2 equivalent^{-1} = 549.11 \, S \, cm^2 \, equivalent^{-1}$$

$$\kappa = \frac{\Lambda c}{1000} = \frac{549 \times 10^{-7}}{1000} \, S/cm = 5.5 \times 10^{-8} \, S/cm = 0.055 \, \mu S/cm$$

This theoretical value is difficult to obtain experimentally because atmospheric CO_2 is readily

absorbed into water. The conductivity of CO_2 in water was measured and found to be 1.05 μS/cm

at 25 °C [8,10]. When other ionic contaminants are also present in water, the conductivity value will increase further. For example, when 1 ppm of Ca^{++} ions, or Na^+ ions, is present in water ($c \approx$ 5×10^{-5} equivalents per liter), the conductivity of this water would be approximately 3 µS/cm. In addition to the 1 µS/cm from CO_2 absorption, the final value for the conductivity of water would be 4 µS/cm. Thus, the value of conductivity is an indicator for the purity of water if this value is properly determined. To ascertain the accuracy of the measured value, low conductivity standards are needed for calibration and for quality assurance of the purity of water (see Sec. 5.3).

2. General Scheme of the Electrolytic Conductivity Measurement

The conductivity of a solution is determined by measuring the resistance of a solution in a given cell, using either the AC or DC method, and then calculating the conductivity from Eq. (1). The AC method uses a Wheatstone bridge for measuring the resistance, and the DC method uses a DC digital voltmeter (DVM). The details of the AC and DC methods will be described in Sec. 3. The electrolytic conductivity of a solution is affected by the temperature of the solution, the carbon dioxide content of the solution, and the amount of evaporation or transpiration that occurs prior to the measurement.

2.1 Temperature Control

Electrolytic conductivity is very sensitive to changes in the temperature of the solution. The conductivity of inorganic electrolytes changes about 2 % for each degree Celsius at room temperature [7]. A 0.005 °C fluctuation will cause a ±0.01 % change in conductivity. Therefore, good temperature control is required for an accurate measurement of the conductivity of a solution.

To achieve the required temperature control, the conductivity cell is placed in a constant temperature bath. Mineral oil is typically used as the bath fluid. The equipment used at NIST for monitoring the temperature of the constant temperature bath consists of a quartz thermometer

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connected to a frequency counter with a digital readout. The quartz thermometer and frequency

counter were calibrated by comparison to the NIST standard platinum resistance thermometer

(SPRT) and have an uncertainty not greater than 0.002 °C. When the temperature bath is correctly

adjusted, the temperature can be controlled to ±0.002 °C.

When the conductivity cell is designed such that there are large electrodes in bulbs at the end

of a long narrow tube, most of the resistance is contributed by the narrow tube. The effect of

temperature, t, on the cell constant is given by [7]

$$\left(\frac{\partial K_{cell}}{\partial t}\right)\frac{1}{K_{cell}} \approx \left(\frac{\partial l}{\partial t}\right)\frac{1}{l} - \left(\frac{\partial A}{\partial t}\right)\frac{1}{A} = \alpha_g - 2\alpha_g = -\alpha_g \tag{10}$$

where $\alpha_g = 3.6 \times 10^{-6}$ °C^{-1}, the thermal expansion coefficient of Pyrex glass. For the whole range of

temperatures, 0 °C to 50 °C, the change in K_{cell} is approximately 0.02 %. This method of

determining the cell constant has been used in our laboratory for determining the temperature effect

on the cell constant of an absolute conductivity cell.

2.2 Carbon Dioxide Contribution

The electrolytic conductivity of pure water equilibrated with atmospheric carbon dioxide

is typically taken to be 1 µS/cm [9]. Carbon dioxide will dissolve in solution producing H$^+$ and

HCO$_3^-$, which will contribute to the conductivity of the water. The contribution of these ions to

the conductivity is referred to as κ_{CO_2}. The concentration of these ions is dependent on the

atmospheric pressure, ventilation, and number of people in a particular laboratory. When

conditions vary, the uncertainty in κ_{CO_2} is taken as 20 % of the typical value for the conductivity

of water in equilibrium with atmospheric CO$_2$. Therefore, for an aqueous KCl solution, the

uncertainty in κ_{CO_2} is estimated to be ±0.2 µS/cm. The lower pH of the HCl solution suppresses carbon dioxide dissociation.

In a nonaqueous-aqueous solvent, carbon dioxide dissolution and hydrogen ion conductivity is much less than that in water. Typically, the variation in κ_{CO_2} is less than ±0.1 µS/cm [9].

When NIST electrolytic conductivity SRMs are prepared, the solution is shaken for several days to facilitate equilibration with carbon dioxide prior to bottling. The certified value of the batch includes the contributions to the conductivity of all ions present in the solution, including HCO_3^-. Therefore, the user does not need to degas the solution prior to use. By equilibrating the solution with atmospheric carbon dioxide, the need to prepare and measure the solution in a carbon dioxide free environment is avoided, making the SRMs easier to use.

2.3 Evaporation and Transpiration

Transpiration and evaporation both cause the conductivity of a solution to increase. Transpiration, the passage of solvent through containers, has been observed in this laboratory for bottles made of low-density polyethylene (LDPE). Solutions that will be stored for more than a day, such as an SRM, should be packaged such that minimal transpiration occurs over the time of storage. In this laboratory, glass bottles are used for SRMs because the amount of transpiration, if any, is unnoticeable. For solutions that will be used immediately after they are prepared, such as primary standards, transpiration is much less of a concern since long-term storage is not an issue.

Evaporation may occur as a result of the measurement process, or as a result of a poor packaging technique. When preparing the solution or filling the cell, evaporation needs to be minimized. For primary standards, accurate concentration is necessary for accurate

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measurement. This is much less of a concern for electrolytic conductivity SRMs, which are certified based on conductivity and not on exact concentration. Filling the cell, with any solution, will cause slight evaporation of the solution. Evaporation may also occur if the cap of the bottle is not completely closed, or if the cap relaxes and loosens with time. In this laboratory, such problems have been noted for glass bottles with polypropylene caps and glass bottles with Bakelite caps. However, serum bottles and ampoules do not appear to have a problem with evaporation when they are sealed.

To obtain an accurate measurement of the conductivity of a solution, evaporation and transpiration must be minimized. Over time, if evaporation and transpiration due to the packaging of the solution occurs, the accuracy of the conductivity measurement will be compromised.

3. Absolute Conductivity Measurements

Absolute conductivity measurements are performed using conductivity cells, the cell constant of which is determined by basic standards only (electrical and physical). The two absolute methods, AC and DC, use different types of cells and instrumentation. The choice of the AC or DC method will be described in Sec. 3.4. The absolute conductivity measurement has been used at NIST to determine the conductivity of molality-based primary standards. These primary standards may then be used to calibrate other types of cells (section 4).

3.1 Primary Standards

Establishment of conductivity values for primary standard solutions requires the use of the absolute method, and is the primary purpose of the absolute method. Both the AC and DC methods, described in the following sections, have been used to measure the conductivity of the primary

standards. The work performed in this laboratory [8, 10-12], and described in this report, has taken several years. The data are listed in Tables 1-3.

Table 1. Definition of Demal for 0.01D, 0.1D, and 1.0 D KCl Solutions

Demality	grams of KCl per kilogram of
0.01	0.745819[6]
0.1	7.47458[6]
1.0	71.1352[8]

Table 2. Electrolytic Conductivity Values for 0.01D, 0.1D, and 1.0 D
KCl Solutions* and Water, ITS-90 Scale

$t/°C$	$10^4 \, \kappa / \, (\mu S/cm)$			
	0.01 D KCl[11]	0.1 D KCl[11]	1.0 D KCl[8]	H_2O[11]
0	773.09	713.46	65 135	0.58
5	891.17	819.97	73 860	0.68
10	1 014.2	930.82	82 871	0.79
15	1 141.7	1 045.6	92 136	0.89
18	1 220.1	1 116.1	97 804	0.95
20	1 273.2	1 163.8	101 620	0.99
25	1 408.4	1 285.1	111 300	1.10
30	1 546.8	1 408.9	121 110	1.20
35	1 688.0	1 535.0	131 050	1.30
40	1 831.5	1 662.8	141 080	1.40
45	1 976.9	1 791.9	151 150	1.51
50	2 123.8	1 921.9	161 240	1.61

* Values of conductivity for KCl solutions do not include solvent conductivity

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Table 3. Electrolytic Conductivity Values for the Molality-Based Primary Standard KCl Solutions*
0.01 mol/kg, 0.1 mol/kg, and 1.0 mol/kg, ITS-90 Scale

$t/°C$	$10^4 \, \kappa / \, (\mu S/cm)$						
	0.01 mol/kg		0.1 mol/kg		1.0 mol/kg		water
	value[10]	$2u_c$[12]	value[10]	$2u_c$[12]	value[8]	$2u_c$[12]	value[10]
0		0.23		2.85	63 487	25	0.58
5		0.27		3.27	72 030	29	0.68
10	1 013.95	0.30		3.72	80 844	32	0.79
15	1 141.45	0.34	10 437.1	4.2	89 900	36	0.89
18	1 219.93	0.37	11 140.6	4.5			0.95
20	1 273.03	0.38	11 615.9	4.6	99 170	40	0.99
25	1 408.23	0.42	12 824.6	5.1	108 620	43	1.10
30	1 546.63	0.46	14 059.2	5.6	118 240	47	1.20
35	1 687.79	0.51	15 316.0	6.1	127 970	51	1.30
40	1 831.27	0.55	16 591.0	6.6	137 810	55	1.40
45	1 976.62	0.59	17 880.6	7.2	147 720	59	1.51
50	2 123.43	0.64	19 180.9	7.7	157 670	63	1.61

*Values of conductivity for KCl solutions do not include solvent conductivity

Primary standards are used for calibrating conductivity cells. The chief requirement for the

standard is accuracy. The factors affecting the accuracy of the primary standards include stability of

the chemical, purity of the solute and solvent, and concentration of the solution. Potassium chloride

was chosen as the solute [1-6] because KCl is stable and easily purified. Water is used as the

solvent because it is also stable and easily purified. These two factors are very important for

maintaining uniformity and repeatability when the solutions are prepared in different laboratories,

so that the results can be accurately compared. For high accuracy measurements, the concentration

of the primary standard solutions should be accurate to at least 5 places.

Currently, three primary standards at three temperatures are recommended by IUPAC [13]

and Organization Internationale de Metrologie Legale (OIML). These primary standards are based

on the measurements of Jones and Bradshaw [4]. The primary standards have concentrations defined by the so-called demal (D) scale, which is defined as an exact mass of KCl in an exact mass of water. This scale is not related to any other concentration scale. The demal unit is defined at three concentrations only (Table 1): 0.01 D, 0.1 D, and 1.0 D.

NIST redetermined the primary standards adopted by IUPAC and determined a new set of molality-based primary standards. The measurements of the primary standards by Jones and Bradshaw were performed over 60 years ago and several basic standards have been changed. Moreover, the demal scale lacks a direct relationship to the common units of concentration and to the units used in solution chemistry. The original values have been adjusted for changes in the basic standards to obtain the values currently adopted by IUPAC. In addition, the conductivities of the recommended demal standards are only determined at three temperatures. Therefore, NIST not only redetermined the set of primary standards adopted by IUPAC to reconfirm its value, but also determined a set of molality-based primary standards available at temperatures from 0 °C to 50 °C at 5 °C intervals and at 18 °C (Table 3) to expand the applicability of primary standards.

The molality-based primary standards developed at NIST were prepared using potassium chloride and water. Molality, mol/kg, is defined as the amount of solute in one kilogram of solvent *in vacuo*. Molality-based primary standards at three concentrations expressed in molality (0.01 mol/kg, 0.1 mol/kg, and 1.0 mol/kg) in the temperature range of 0 °C to 50 °C have been proposed to OIML and to the IUPAC for adoption [10,12].

3.2 AC Absolute Method

The AC absolute cell was designed and constructed at NIST for the measurement of the 0.01 D and 0.1 D primary standards, and the 0.01 mol/kg and 0.1 mol/kg molality-based primary

standards [6,10,11]. This AC absolute cell, its design, instrumentation, and measurement method, are described in the following sections.

3.2.1 Cell Design

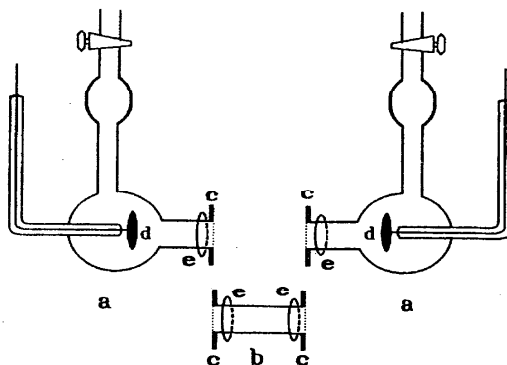The AC absolute cell, shown in Fig. 1, is a Jones type cell with a removable center tube.

Figure 1. AC absolute conductivity cell: a, a – electrode chambers (half-cells); b – removable center extension tube; c, c – flanges; d, d – platinum disk electrodes; e, e – O-rings. The mating flange ends are held together by a C-shaped Bakelite band (not shown) so that lateral movement is prevented.

The design of this cell allows determinations of the conductivity of a solution from basic standards. No calibration of the cell is necessary. The details of cell construction [9,10] are briefly described as follows. A length of precision-bore 1 cm I. D. Pyrex tubing, with uniformity certified by the manufacturer, was cut into 3 sections. A prefabricated flange, c, with an I. D. of 1.3 cm, O. D. of 2.5 cm, and thickness of 0.65 cm was epoxied into each of the tubes such that the face of the flange was flush with the cut end of the tube. Then, each flanged end was ground to optical flatness. The unflanged end of each of the singly flanged tubes was joined to the corresponding electrode chamber, a, each of which contained a 2 cm platinum disk electrode, d. The electrodes were gold soldered to a 2 mm platinum wire, which extended through a graded-glass seal. To assemble the

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cell, the mating flange ends are held together by a C-shaped Bakelite band which can be slightly enlarged with a little pressure, such that the two flanges fit snugly into it, preventing the flanges from moving laterally. Lateral and rotational movements are prevented by a Bakelite two-plate assembly tightened together with four nylon screws and nuts. A rubber O-ring, e, is inserted between each plate and the rear side of the flange. The tube b of the cell is removable, and its dimensions (length and internal diameter) were determined by the Length and Mass Division of NIST (presently, length is determined by the Precision Engineering Division; mass is determined by the Automation Production and Technology Division).

Since the cell constant in a Jones-type conductance cell is determined by the lines of force between the two electrodes, the center section of the tube may be removed in order to shorten the distance between the electrodes, thereby reducing the resistance. Subsequently, the same section may be put back, lengthening the distance and increasing the resistance, provided that the lines of force are not disturbed. Thus, there are essentially two cells: one is with the center tube b, and the other is without the center tube b. When the conductivity, κ, of a solution with fixed concentration is measured with the two cells, we will obtain the resistance of the solution in the cell with the center tube, R_w,

$$R_w = \frac{K_{cell,w}}{\kappa} \qquad (11)$$

and the resistance of the solution in the cell without the center tube, R_N,

$$R_N = \frac{K_{cell,N}}{\kappa} \qquad (12)$$

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where $K_{cell,W}$ and $K_{cell,N}$ are the cell constants with and without the center tube, respectively. Similarly, R_W and R_N are measured resistances when using the cell with the center tube and without the center tube, respectively.

Equation (11) and Eq. (12) may be combined by subtracting R_N from R_W and solving for κ:

$$\kappa = \frac{K_{cell,W} - K_{cell,N}}{R_W - R_N} = \frac{K_{cell,T}}{R_W - R_N} \tag{13}$$

The cell constant of the center tube, $K_{cell,T} = l/A$, is determined by physical measurements of l and A and is equal to $K_{cell,W} - K_{cell,N}$. All the quantities on the right-hand side of Eq. (13) are known by means of physical measurement. Therefore κ is absolutely determined and values for $K_{cell,W}$ and $K_{cell,N}$ can then be calculated from Eq. (11) and Eq. (12).

3.2.1.1 Cell Cleaning Process

When the cell is newly constructed, it is cleaned with chromic acid cleaning solution, rinsed with water, soaked in a 6 mol/L HCl solution for 1 h, washed with water, soaked in distilled water overnight, and dried at room temperature. In cases where the HCl soaking, water washing, soaking, and vacuum drying do not remove the last traces of adsorbed chromate ions, the process must be repeated. (Strong acids and organic solvents have been tried as a replacement for chromic acid cleaning solution, without success.) After the cell is thoroughly clean and dry, it is assembled and filled with a standard KCl solution. If no leak is detected at the joints after the filled cell stands for 1 h, the cell is put into the bath for 30 min to 40 min until the solution reaches thermal equilibrium with the bath temperature. The reading is then recorded. If no drift is noted over a 1 h period, the cell is emptied and refilled to obtain measurements in triplicate. If the deviation of the results is less than 0.01 % and random, the mean is taken as the final result. If the deviation shows a trend toward increasing or decreasing resistance, there are two probable causes: cell contamination and loss of

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water from the solution by evaporation. Cell contamination is generally caused by adsorption of foreign substances on the cell walls and/or electrodes. There is no easy way out of this except either to repeat the experiment until the foreign substances are leached out and the readings are constant, or to repeat the cleaning process. If the drift is due to concentration increase by evaporation, a new solution will generally cure it.

The procedures for changing from one concentration to another and/or for replacing the center tube of the cell are similar. The cell is taken out from the bath, the outside wall of the cell and the whole assembly are washed with soap solution and rinsed with water. The inside of the cell is flushed with distilled water continuously for about 30 min. The whole unit is dried with paper towels and is disassembled. The joints of the cell are cleaned with soap and water. When everything is dry, they are re-assembled. Caution is always exercised to prevent the oil on the outside of the cell from creeping inside. If this occurs, the cleaning process must be repeated

3.2.2 Instrumentation

The AC method for conductivity measurement consists of a constant temperature bath and the resistance measurement instrumentation. The constant temperature bath used when measuring the primary standards [11] is briefly described below. The bath consisted of a rectangular, steel, open-top box surrounded by a wood cabinet with a hinged cover that can be opened or closed. The space between the sides of the steel box and the wood cabinet was insulated with glass wool. Within the steel box were vertical, open-ended rectangular walls around which a piece of copper tubing was looped. The tubing led to the outside of the wood cabinet for connection to a temperature-controlled fluid. A stirrer was mounted on the inside wall to provide good circulation. Studs were mounted in the front side of the steel box to allow for support and manipulation of the conductivity cell. Twenty gallons of petroleum oil were used as bath fluid, and the oil was changed

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every 6 months to 8 months. Water was circulated through the copper coil and back for cooling by an auxiliary constant-temperature bath. The heating is facilitated with a quartz heater submerged into the bath. The whole unit was connected to a proportional temperature control unit. A thermistor is used as the sensor for the temperature controller. A quartz thermometer and frequency counter are used as the bath temperature indicator.

The AC instrumentation [10,11] is described as follows. The AC measurement uses a Jones bridge [14,15], which is a Wheatstone bridge with capacitance compensation that is specifically designed for conductivity measurements. The Jones bridge is equipped with a capacitor and resistor in parallel to balance the impedance of the conductivity cell. The bridge also employs a Wagner ground to minimize the effects of stray capacitance on the accuracy of the null point. The ratio-arms are held exactly equal.

Alternating current is supplied to the bridge by a signal generator. The signal generator can be operated from 20 Hz to 15 kHz. The normal operating range of frequency, ω, is 1 kHz to 5 kHz. The resistance is corrected for the effect of polarization by plotting R versus ω^{-1} and extrapolating to $\omega = \infty$ [7]. The signal generator was modified by floating the secondary of the output transformer to obtain an ungrounded output, which is required to make use of the Wagner ground of the Jones bridge. A single-ended (unbalanced) output was obtained from a secondary winding of the output transformer and was used as the phase reference for the detector. The applied AC voltage to the bridge is 1.2 V RMS. A differential input preamplifier, tuned amplifier, and oscilloscope are used in the detector circuit. The differential input of the preamplifier preserves the balance of the Wagner ground and eliminates the need for an input transformer. The tuned amplifier is used in the bandpass mode at a Q (Q is the ratio of the frequency to the bandwidth, thus, the smaller the bandwidth, the larger the Q) of 10 to 50, to attenuate the second and higher harmonics at the null

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point. The output of the tuned amplifier and the reference signal from the signal generator are connected to the vertical and horizontal inputs of the oscilloscope, respectively. The displayed pattern on the oscilloscope is a Lissajous figure and is used to indicate both capacitive and resistive balance of the bridge simultaneously [16]. (The technique was superior to using the in-phase and quadrature output meters of the lock-in amplifier to indicate resistive and capacitive balance of the bridge.)

With this setup, a 0.001 % change in cell resistance may be detected on the oscilloscope. Hence, a change of 0.001 °C in the bath temperature (0.002 % in R) can be observed. The uncertainty in the null point measurement did not contribute significantly to the overall uncertainty of the measurement of the resistance of the primary standard.

3.2.3 Measurement

In the AC measurement of conductivity, the cell will generally have an impedance Z_1 that is not purely resistive. However, there are other sources of impedance such as the Parker effect [17] and the effect of a conducting thermostat medium [14]. These effects can be avoided by proper cell design.

When measuring the resistance of a solution, the combination of the solution conductivity and cell constant is chosen such that the measured resistance is within the optimum range of resistances for the bridge. The optimum range for resistances when using the Jones bridge is $1\ 000\ \Omega < R < 10\ 000\ \Omega$. The Jones bridge has five decade resistors plus the slide wire resistor. The maximum uncertainty of the nominal readings of the dials is less than 0.005 % as stated by the manufacturer.

The cell is placed into the conductivity bath for about 30 min, so that the solution in the cell can reach thermal equilibrium with the temperature of the bath. Resistance readings are taken at 1

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kHz and 2 kHz at 10 min intervals to determine that the solution's temperature is constant. The polarization correction is made by plotting the measured resistance, R, vs. ω^{-1} and extrapolating to $1/\omega = 0$ [7]. The resistance of the solution is then calculated by correcting the extrapolated resistance for the lead resistance (from the electrodes to the binding posts of the bridge). If the resistance continuously drifts upward or downward for 30 min, this indicates that the concentration of ions in the solution is changing, or that the temperature is changing. In this instance, the measurement should be stopped, the cause of the drift determined, and the measurement repeated.

3.3 DC Absolute Method

At NIST, the DC absolute cell was designed for the measurement of the 1 D primary standard and the 1 mol/kg molality-based primary standard [8]. The DC absolute cell, its design, instrumentation, and measurement method, are described in the following sections.

3.3.1 Cell Design

The DC absolute cell is a four-electrode conductivity cell (Fig. 2). The two inner electrodes are used to measure potential drop and the outer two electrodes are used to measure the applied current, I. In order to eliminate polarization effects, all four electrodes must be reversible to the solution. For primary standard KCl solutions, Ag, AgCl electrodes are suitable.

For an absolute determination of conductivity, the cell constant needs to be determined with the same basic standards (e.g., length measurement) as the AC cell. To accomplish this requirement, a precision bore Pyrex tubing is cut into three pieces, so that the center section of the cell could be removed and that the internal diameter and length of this center section could be measured accurately by physical methods. The two ends of the center section were polished to flatness, while the surfaces of the ends of the other two pieces, which will join with the center section, were ground to a roughness of about 25 μm. A slight gap was formed between the joined

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ends of the tubing to effect a miniscule flow of solution, when the sections are rejoined using a

nylon union. The other two ends of the cut tubing are fused to Pyrex tubing comprising the current

compartments of the cell. A U-shaped capillary separates the current-electrode chamber from the

connecting chamber to minimize the effect of electrolysis products on the measurement. A third

tube is joined at each of the junctions of the center section with the end sections using a nylon-union

tee. These compartments contain the potential leads for the measurements. The final assembly is
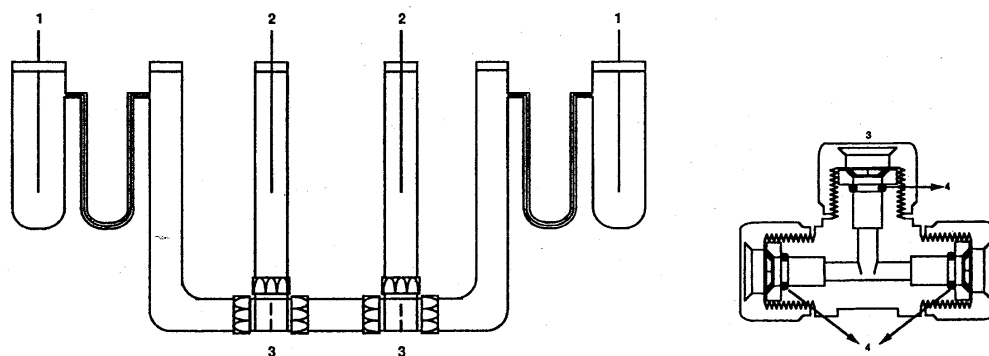
shown schematically in Figure 2.

Figure 2. DC Absolute conductivity cell: 1, 1 – current electrodes; 2, 2 – potential difference
sensing electrodes; 3 – nylon tee joints; 4,4 – O-rings.

Cleaning of the cell when it is newly constructed, and when changing concentrations, is the

same as described in Sec. 3.2.1.1

3.3.2 Instrumentation

The DC method is much simpler in principle than the AC method and is determined by

Ohm's law [8]. A high precision digital voltmeter (DVM), an accurate standard resistor, and a

constant current supply are needed for the measurement of R. Both the DVM and the standard

resistor were calibrated by the Electricity Division at NIST. The constant current supply can

provide current from 25 μA to 250 mA and has a stability of ±0.005 % over 14 h. A schematic

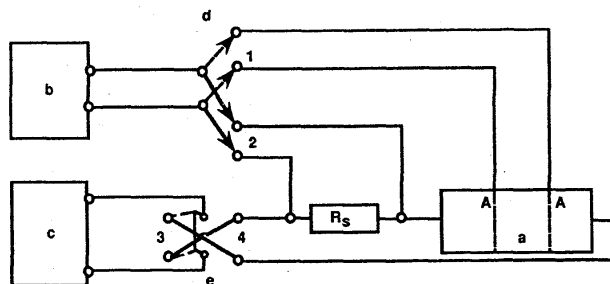diagram of the operating circuit is shown in Fig. 3.

Figure 3. Schematic of DC Operating and Switching Circuitry: a – conductivity cell with gaps A, A; b – digital voltmeter; c – constant current supply; d – switch with position 1 and 2; e – switch with position 3 and 4; R_s – standard resistor

With switch **d** in the **2** position and switch **e** in the **3** position, current flows through the standard

resistor and the conductance cell, and the IR drop across the standard resistor, E_s, is measured by the

DVM as

$$E_s = IR_s \tag{14}$$

where R_s is the resistance of the standard resistor and I is the current. I is thus determined. Moving

switch **d** to the **1** position while switch **e** remains in the **3** position effects the measurement of the

voltage between the potential electrodes in the conductance cell, E_T,

$$E_T = IR_T \tag{15}$$

where R_T is the resistance of the solution in the conductance cell. Switching **e** to the **4** position

reverses the flow of current and the polarity of the current electrodes. A data point at a singe

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current consisted of four measurements as shown in Table 4. Any difference between the standard

redox potentials, E°, of the potential difference-sensing electrodes was eliminated by reversing the

direction of the current, I, and averaging the magnitudes of the two measured potential differences.

This averaged potential difference, ΔE, was related to conductivity by

$$\kappa = \frac{K_{cell,T}}{R_T} = \frac{I_c}{\Delta E} K_{cell,T} \qquad (16)$$

where $K_{cell,T}$ is the cell constant of the center tube, and R_T is the resistance of the solution in tube.

Table 4. Measurement Sequence[8]

Measurement	Switch d	Switch e
1	2	3
2	1	3
3	1	4
4	2	4

Two pairs of matched Ag, AgCl electrodes were used in the conductance cell: one pair for the

current electrodes and the other for the potential electrodes. The preparation and calibration of these

electrodes have been described in conjunction with the pH studies at NIST [18]. All four electrodes

were within ± 0.05 mV of each other. Reversible electrodes are required to eliminate polarization

effects. Ag, AgCl electrodes, appropriate for KCl solutions, were used for all four electrodes to

minimize the effects of electrolysis and polarization.

Two constant temperature baths were used at NIST: an oil bath [10] in which the

temperature could be controlled to ±0.002 °C (described in Sec. 3.2.2) and a water bath [11] in

which the temperature could be controlled to ±0.001 °C to ±0.002 °C for temperatures above

0 °C.

3.3.3 Measurement

After the cell is assembled, and filled with solution, the electrodes are placed in the

appropriate chambers. The whole cell assembly is put into the bath, and its temperature is adjusted

and controlled as designated. Usually, the starting temperature is 25.000 °C, and a steady state is

reached after about 30 min.

The wiring to the electrodes was connected according to the scheme shown in Fig. 3. The

outer electrodes are connected to a constant current supply, **c**. A standard resistor, R_s, is inserted

between an outer electrode and the constant current supply, so that the current passing through the

cell and the R_s is the same (see Fig. 3). The inner electrodes are connected to the digital voltmeter,

b. The gaps, **A,** are the opening for connecting the inner electrodes (Fig. 3). Platinum wires may

serve as the outer electrodes. The inner electrodes are preferably reversible to the electrolyte

solution, such as Ag/AgCl to KCl, in order to eliminate polarization. For a solution without

reversible electrodes, e.g., NH_4NO_3, calomel electrodes with liquid junction may be used to measure

the potential drop across the fixed points **a**. The cell is modified with four side tubes to

accommodate the liquid junction at the inner electrodes, and to minimize the hydrolysis effect at the

outer electrodes.

It took approximately 3 s for a reading, and there were four readings for a selected current,

two each for each direction (as described in Sec. 3.3.2). Each data point was taken as the mean of

three different currents. At each temperature, the current flowed through the cell for approximately

30 s. Thus, the power dissipated in the cell was less than 1 mW, and its effect was much smaller

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than a millidegree per second change for the solution. Therefore, there is no significant heating effect.

3.4 AC vs. DC Method

For absolute measurement of conductivity, there are limitations of dimension for the constant temperature bath and for the conductivity cell. Hence, the range of cell constants is limited. Thus, the AC method is preferred for solutions of low conductivity and high resistance due to lower experimental uncertainties. The DC method is preferred for solutions of high conductivity, and hence low resistance. For the AC method, an optimum range of resistance is required for the best accuracy. Typically, an error in the resistance of a few hundredths of an ohm would result from either the bridge or the lead resistance. For example, if R is 100 Ω, an error of 0.05 Ω absolute is equivalent to an error of 0.05 % relative. If R is 1000 Ω, an error of 0.05 Ω absolute is equivalent to an error 0.005 % relative. Therefore, a larger cell constant, which is difficult to achieve, is necessary when using the AC method to minimize these effects. When the DC method is used, errors due to the bridge and the lead resistance are eliminated. Because the potential measured does not include the leads, the lead resistance is eliminated. The accuracy of a voltmeter can reach 10^{-7} to 10^{-8} V. An applied current may be selected from 10^{-5} to 10^{-2} A. For a given cell constant, κ can be varied a thousandfold and can be determined without sacrificing accuracy.

The conductivities of the 1 mol/kg molality-based primary standard and the 1 D primary standard were determined using the DC method (Table 2-3). The conductivities of the 0.01 mol/kg and 0.1 mol/kg molality-based primary standards and the 0.01 D and 0.1 D primary standards were determined using the AC method (Table 2-3).

3.5 Error Analysis for Primary Standards

The error analysis performed at NIST for the conductivity measurements of the molality-based primary standards using the AC and DC measurement methods [6,8-11] is briefly discussed below. The errors calculated for each value of conductivity [12] are listed in Table 3. The values for the conductivity of the primary standards (Table 3) were calculated using Eq. (17), which is a polynomial fit of the values for conductivity at each temperature:

$$\kappa = a + bt + ct^2 + dt^3 \qquad (17)$$

The values for a, b, c, and d are given in Table 5. The standard uncertainty of the differences between the smoothed values of κ and the discrete values of κ are 0.0046 %, 0.0126 %, and 0.0145 % for the 0.01 mol/kg, 0.1 mol/kg, and 1.0 mol/kg molality-based KCl primary standards, respectively.

Table 5. Parameters in the Polynomial Fit for Electrolytic Conductivity Versus Temperature[12]

Molality, mol/kg	Parameters			
	a	b	c	d
0.01	0.0772921	2.30846×10^{-3}	1.07715×10^{-5}	-5.84084×10^{-8}
0.1	0.711685	2.09002×10^{-2}	8.99144×10^{-5}	-5.07124×10^{-7}
1.0	6.34882	1.6913×10^{-1}	6.00781×10^{-4}	-3.83702×10^{-6}

The uncertainty in the measurements of $K_{cell, T}$ was based on the measurement of the length and diameter of the tube. The values for the standard uncertainty are 0.0065 % for 0.01 mol/kg and 0.1 mol/kg, and 0.0085 % for the 1.0 mol/kg molality-based primary standard.

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The effect of changes in temperature on $K_{cell, T}$ may be calculated from Eq. (10), which applies to both AC and DC measurements. For the AC measurements, the values of κ for each molality were calculated using the corrected value of $K_{cell, T}$. The uncertainty in this correction for AC measurements was negligible. For the DC measurements, no correction was applied to $K_{cell, T}$. The standard uncertainty is taken as 0.0052 % for the DC measurements, based on the estimated change in $K_{cell, T}$ with temperature.

The uncertainty in the measurement of temperature, arising from the calibration of the thermometer, was ±0.002 K. The temperature coefficient at each temperature was determined directly from the smoothed polynomial fit of κ versus t. The largest temperature coefficient, which was at 0 °C, was multiplied by ±0.002 K. The standard uncertainty, ±0.0034 %, was treated as a uniform probability distribution, and has been divided by $3^{\frac{1}{2}}$ [19].

The effect of impurities in the KCl for the primary standards was estimated to contribute an uncertainty of 0.0025 % to the conductivity. The standard uncertainty due to evaporation of the primary standard solutions during transfer to the conductivity cell is estimated to be 0.0025 %.

The resistors in the AC conductivity bridge were calibrated and the uncertainty in this calibration, 0.001 %, was treated as a uniform probability distribution. The standard uncertainty was thus taken as 0.0057 %. The standard uncertainty of the DC measurements of current and potential was taken as 0.00061 %.

The uncertainty in the solvent correction was taken as 0.2 μS/cm. The standard uncertainty, treated as a uniform probability distribution, was less than 0.0015 % in all cases.

The uncertainties for each primary standard were calculated as the root sum of squares. The actual uncertainties were conservatively estimated to be 0.03 % for the 0.01 mol/kg primary

standard, and 0.04 % for both the 0.1 mol/kg and 1.0 mol/kg primary standards. Uncertainties

calculated for each primary standard at each temperature are given in Table 3.

4. AC Conductivity Measurement With Other Cells

As mentioned in Sec. 3, the primary standards are used to calibrate conductivity cells.

Absolute cells are used when the best possible accuracy is needed. Some solutions, such as

SRMs, do not require the high accuracy measurement that primary standards require. For SRMs,

Jones and Daggett cells [7], which are calibrated using primary standards, are used for making

the resistance measurements.

4.1 Cell Construction

The Jones and Daggett cells used at NIST are made of borosilicate glass and use platinum

electrodes. Jones cells are usually composed of two glass bulbs, each containing a platinum disk

electrode, separated by a piece of glass tubing to give a large cell constant (Fig. 4).
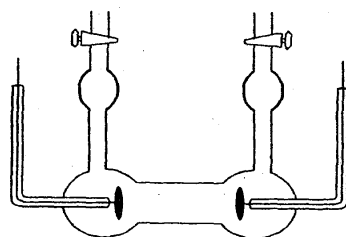

Figure 4. Jones Cell: Jones cell is similar to the AC absolute cell except that it does not have a
removable center tube.

To minimize evaporation when filling the cell, the solution is poured through a funnel and into

the cell. Less evaporation occurred with this type of filling than with the other methods

examined in this laboratory.

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Daggett cells consist of an Erlenmeyer flask that is connected to a glass bulb containing the electrodes (Fig. 5). The use of the Erlenmeyer flask facilitates filling of the cell.
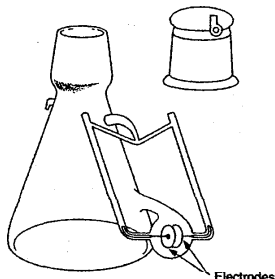

Figure 5. Daggett cell: diagram is similar to the Jones cell, except that an Erlenmeyer flask is attached to facilitate filling of the cell.

However, an Erlenmeyer flask can only be attached to cells with small cell constants due to design problems. Daggett cells are typically used for low conductivity solutions.

All of the Jones and Daggett cells used at NIST were made on-site. Several items must be considered when making a conductivity cell. The cells should contain no rough edges and ridges. Any microcracks where the solute could be trapped must also be eliminated. When adding a solution to the cell, any trapped solute would dissolve and the concentration of ions, and therefore the conductivity, would change. Two types of microcracks were observed with commercial cells: (1) at the joining of the platinum wire to the disk, and (2) at the joining of the platinum to the glass. The lack of a smooth surface when spot welding the platinum disk onto the platinum lead left small cracks where KCl could be trapped. These cracks were eliminated by using gold to smooth out the surface. Because Pyrex does not wet platinum, the glass would pull away from the lead leaving small cracks where KCl could be trapped. This problem was solved

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by using a type of soda lime glass that does wet platinum. A graded seal was used to fuse the soda lime glass to Pyrex.

4.2 Calibration of Cells

Presently, the Jones and Daggett cells at NIST have cell constants ranging from about 0.05 cm^{-1} to 110 cm^{-1}. The standards used for calibrating these cells must be accurately prepared, as was mentioned in Sec. 3.1 for the primary standards. Solutions should be used within several hours of preparation to minimize evaporation and transpiration. Several different standard solutions should be used and, when possible, at least two of the solutions should have concentrations that are one order of magnitude different. The cell should be calibrated at the temperature, or temperatures, that will be used for measuring the conductivity of solutions.

4.2.1 Cells With Constants Greater Than 1.5 cm^{-1}

For calibrating a cell at 25 °C, molality-based primary standards are available in the conductivity range of approximately 1 400 µS/cm to 110 000 µS/cm. The combination of solution and cell should result in a resistance in the optimum range. This is easily achieved for cells with $K_{cell} > 1.5$ cm^{-1}. For example, a cell with $K_{cell} = 2$ cm^{-1} would be calibrated with the primary standard having a molality of 0.01 mol/kg which has a conductivity of 1409.33 µS/cm, including the solvent conductivity. In this example, the measured resistance would be about 1 400 Ω. A cell with $K_{cell} = 110$ cm^{-1} would be calibrated with the primary standard having a molality of 1.0 mol/kg. The measured resistance would be about 1 000 Ω.

4.2.2 Cells With Constants Less Than 1.5 cm^{-1}

As mentioned above, for calibrating a cell at 25 °C, primary standards are available in the conductivity range of approximately 1 400 µS/cm to 110 000 µS/cm. If $K_{cell} \leq 1.5$ cm^{-1}, the resistances of the primary standards will be in the range of 900 Ω to 10 Ω. The accuracy of a

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resistance measurement would be compromised because an uncertainty of ±0.1 Ω in the measured resistance would cause a 0.014 % to 1 % uncertainty in conductivity. If the primary standard is used for calibrating a cell with $K_{cell} \approx 0.1$ cm^{-1}, the uncertainty will increase according to Eq. (4). Therefore, working solutions must be used.

At NIST, working solutions are prepared for calibrating conductivity cells by estimating the amount of KCl necessary to give the desired conductivity. The resistance of the working solution is then measured in a cell that was calibrated with a primary standard. The conductivity of the working solution is calculated from Eq. (4). The resistance of the same working solution is then measured in the cell to be calibrated. Since the conductivity of the working solution is known, the cell constant may be calculated from Eq. (4).

Some workers in this field employ the Onsager limiting law equation [5,20] for KCl as a function of concentration to prepare secondary standards of the desired conductivity. The equivalent conductivity is calculated for the low concentration of aqueous potassium chloride so that a solution of low conductivity, and optimum resistance, may be used to calibrate the cell. The equivalent conductivity of KCl solutions having concentrations less than 0.05 moles/L may be calculated by

$$\Lambda_{KCl} = 149.83 - 95.09\sqrt{c} + 38.66c \log c + 183.9c \qquad (18)$$

where c has units of mol/L and Λ_{KCl} has units of Sm^2/mol. Equation (18) is based on the literature values for $\Lambda°$ [5] and has been corrected for the change from international ohm to the absolute ohm, the change 1948 IPTS units to 1990 IPTS units, the change in the liter unit, and changes in the atomic masses of K and Cl. The electrolytic conductivity is calculated from Eq. (5). Thus, for a KCl solution of molality 0.0001 mol/kg, $\kappa = 14.888$ μS/cm, not including the solvent conductivity.

If K_{cell} is approximately 0.05 cm^{-1}, then R is approximately 3 400 Ω, which is in the range of optimum resistance. This calibrating equation may yield reasonable accuracy provided the preparation and measurement of the solution are done with pure water and under a CO_2 free atmosphere. Under these conditions, the solvent conductivity correction is near the theoretical value, i.e., 0.055 μS/cm. Otherwise, the solution conductivity must be corrected for a solvent conductivity of 1.1 μS/cm with an uncertainty of ±0.1 μS/cm to ±0.3 μS/cm. This solvent correction would cause an uncertainty of 7 % for a solution having $\kappa = 14.888$ μS/cm.

HCl solutions may also be used for calibrating a cell that has a low cell constant. The theoretical equation [21] for calculating the conductivity of dilute HCl can be written as:

$$\Lambda_{HCl} = 426.16 - 158.68\sqrt{c} + 185.60c \log c + 500c \qquad (19)$$

At 0.0001 mol/L, κ is 42.46 μS/cm for a cell with $K_{cell} \approx 0.05$ cm^{-1} and the resistance measured would be approximately 1 200 Ω. Since the HCl solution has a lower pH than an aqueous KCl solution, CO_2 dissociation is suppressed. Therefore, the uncertainty due to the solvent correction is much smaller. In a carbon dioxide free environment, Eq. (19) yields reasonable accuracy.

4.3 Measurement and Instrumentation

In general, the Jones and Daggett cells are used at NIST to measure the conductivity of SRMs. Measurements made to calibrate the cell or to determine the conductivity of a solution use the instrumentation as described for the AC absolute method (Sec. 3.2.2 and Sec. 3.2.3).

When first constructed, the cell is cleaned as described in Sec. 3.2.1.1. Prior to a measurement, the cell may be cleaned by soaking with water and drying under clean air, argon, or nitrogen. A clean, dry cell is typically rinsed 3 times with the solution to be measured prior to filling the cell. In this laboratory, when several solutions are to be measured in a row, such as

when certifying an SRM, cleaning and drying the cell is not practical due to the amount of time required. Rinsing the cell 5 times with the solution to be measured is sufficient to remove any noticeable effects of the solution previously in the cell.

5. Conductivity Standards for Industrial Applications

When the high accuracy of primary standards discussed in Sec. 3.1 is not needed, commercial standards are sufficient. The most common application of conductivity standards is cell calibration. Two types of industrial standards for electrolytic conductivity are available: commercial standards, many of which claim NIST traceability, and NIST SRMs. The standards must be readily available and easy to use.

5.1 Commercial Standards

Commercial standards are available at conductivities from 100 μS/cm to 100 000 μS/cm. The uncertainties of some of these standards can be as high as 0.5 %.

5.2 Standard Reference Materials (SRMs)

To satisfy industrial needs, NIST certifies and issues certifies a series of electrolytic conductivity SRMs. The SRMs may be divided into two groups: aqueous (nominal values of 25 μS/cm, 100 μS/cm, 500 μS/cm, 1 000 μS/cm, 10 000 μS/cm, 100 000 μS/cm, 20 000 μS/cm), and mixed aqueous-nonaqueous (5 μS/cm and 15 μS/cm). The conductivity of these standards includes the solvent conductivity.

All but two of the aqueous SRMs are prepared as KCl in water. The solute for the 25 μS/cm solution is hydrochloric acid. Hydrochloric acid is used for lower conductivity solutions because it suppresses carbon dioxide dissociation at its low pH. The solute for the 20 000 μS/cm solution is NaCl. The use of NaCl was specifically requested by clinical laboratories. When the 20 000 μS/cm

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solution is made with NaCl, the ionic strength of the solution approximates the ionic strength of body fluid.

The two lowest conductivity SRMs are prepared using KCl in 30 % n-propanol 70 % water. These SRMs are discussed further in Sec. 5.2.3.

5.2.1 Preparation and Measurement of SRMs

The SRMs are prepared initially by underestimating the amount of solute needed for a given amount of solvent that will give the desired conductivity. Since the SRMs are certified based on conductivity, the exact concentration of ions, or more specifically KCl, is not critical. Any minor contamination of the bulk solution (prior to certification) will not spoil the SRM. The bulk solution is then shaken for several days to ensure that the solution is homogenous, and to ensure that the solution has equilibrated with atmospheric CO_2. Using the AC method (Sec. 3.2.2 and Sec. 3.2.3) and a calibrated Jones or Daggett cell (Sec. 4), the resistance of a sample of the bulk solution is measured over several hours. If there is no drift in the conductivity, the solution is equilibrated with atmospheric CO_2. The concentration is then adjusted by adding solute or solvent as required to get closer to the nominal value of conductivity.

The solution is bottled, typically yielding 80 units of the SRMs. A stratified random sampling, based on the bottling order, is used to determine which units will be measured. The measurements of these units are randomized so that trends in bottling order and measurement order may be differentiated. The mean value of these units is called the determined value. This determined value is adjusted upward to correct for changes in the conductivity due to evaporation and/or transpiration, and leaching as needed, to yield the final certified value.

5.2.2 Error Analysis for SRMs

The calculation of the certified value for SRMs has recently been reevaluated. For SRMs, the uncertainty consists of 5 components: 1) random variations in the measurement of conductivity, 2) standard uncertainty of the cell constant, 3) resistance measurements, 4) temperature fluctuation observed during the measurements, and 5) carbon dioxide contribution to the conductivity of the solution. Depending on the bottling type, the effects of transpiration, evaporation, and leaching must also be considered. The uncertainties for each SRM are expressed in absolute terms in each SRM certificate. To generalize the uncertainties for all SRMs, most of the standard uncertainties described below are expressed in relative terms, and are only approximations. A complete uncertainty analysis is required for each SRM batch to determine the uncertainty portion of the certified value of the given SRM.

The random variation in the measurement of conductivity is determined from the standard deviation of the mean and is generally less than 0.008 %. The combined standard uncertainty of the cell constant from a complete uncertainty analysis is used as the standard uncertainty of the cell constant.

The standard uncertainty in the resistance measurements is stated by the manufacturer of the conductivity bridge to be ±0.005 % R for $R > 100\ \Omega$ (95 % confidence interval).

The standard uncertainty of small resistances measured with the digital voltmeter, such as the lead resistance, is stated by the manufacturer of the digital voltmeter to be $0.0012\ \Omega$, absolute. The standard uncertainty for temperature is taken as the temperature variation observed while making the resistance measurements, which is typically ±0.002 °C. The standard uncertainty of the lead resistance and temperature is modeled as a uniform probability distribution and is, therefore, divided by $3^{1/2}$.

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The standard uncertainty due to the thermometer calibration has not previously been included in the determination of the uncertainty of a given SRM. The standard uncertainty of the thermometer calibration is typically 0.002 °C for 95 % confidence interval.

The standard uncertainty of the contribution of CO_2 to the total conductivity is estimated from the possible existing conditions in users' laboratories. The concentration of CO_2 is highly environmentally sensitive and, therefore, can vary due to changes in temperature, atmospheric pressure, and laboratory ventilation. In addition, the CO_2 concentration in a laboratory is higher if more people are in the laboratory. The variation in concentration of CO_2 is estimated to give a variation of ±0.2 μS/cm, absolute, in solvent conductivity. This uncertainty is also modeled as a uniform probability distribution.

Transpiration and evaporation are major concerns when determining the value of an SRM. Unlike primary standards which should be prepared and used immediately, SRMs may not be used for several months after they are packaged. The appropriate packaging must be chosen to minimize the effects of evaporation and transpiration.

5.3 Low Conductivity Standards

For low conductivity standards, it is important to limit the amount of carbon dioxide absorption into the solution and to reduce the uncertainty associated with this absorption. In order to achieve this, a mixed aqueous-nonaqueous solvent is used.

When an aqueous solution is used, the major concern is the CO_2 content in the atmosphere, which varies from 300 ppm to 600 ppm or higher, from one time and place to another [22]. This variation causes a variation in conductivity of about ±0.2 μS/cm, corresponding to an additional 4 % uncertainty for a 5 μS/cm standard. A mixed aqueous-nonaqueous solvent is desirable, because the CO_2 effect in such a solvent is less than 0.1 μS/cm [9]. Therefore, the 5 μS/cm and

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15 μS/cm SRMs consist of KCl in 30 % n-propanol 70 % water.

NIST has studied solutions of KCl in 30 % n-propanol 70 % water and solutions of benzoic acid (BA) in 30 % n-propanol 70 % water [9]. The 100 % pure n-propanol is obtainable on the open market, and both KCl and BA are available as NIST SRMs. The conductivities of the KCl and BA solutions are linear functions of their concentrations at low concentration. They may be expressed empirically as follows [9]:

$$\kappa_{KCl} = 0.35 + 6.38 \times 10^4 c \tag{20}$$

and

$$\kappa_{BA} = 0.04 + 376 c^{\frac{1}{2}} \tag{21}$$

where c is in the units of molality, mol/kg, and κ is in units of μS/cm. The uncertainty of κ_{KCl} is ±0.01 μS/cm and the uncertainty of κ_{BA} is ±0.2 μS/cm. The temperature effect on the conductivity was also examined and found to be 2.9 %/°C for KCl and 2.6 %/°C for BA at 25 °C [9]. Equation (20) and Eq. (21) may be used to obtain the concentration for the desired standard. A list of the required concentrations in molality and in mass fraction for the round values of standard conductivity is given in the following Table 6.

Table 6. Molality and Mass Fraction (Given in Grams Solute per Kilogram Solution, In Vacuum)

of Low Conductivity Standards in 30 % n-PrOH-H_2O [9]

$\kappa/(\mu S/cm)$	Potassium Chloride (KCl)		Benzoic Acid (C_6H_5COOH)	
	molality/(10^{-3} mol/kg)	w/(g/kg)	molality/(10^{-3} mol/kg)	w/(g/kg)
5.00	0.072 9	0.005 43	0.174	0.021 3
10.0	0.151	0.011 3	0.702	0.085 7
15.0	0.230	0.017 1	1.58	0.193
20.0	0.308	0.023 0	2.82	0.344
25.0	0.386	0.028 8	4.41	0.538

6. Discussion and Conclusion

The standards described in this report have a variety of characteristics and applications. The

primary standards, described here, are used for high accuracy work and are determined absolutely

by physical and electrical means, without any calibration. The uncertainties associated with the

primary standards are low if the solution is kept free of acid fumes and carbon dioxide.

The industrial standards are given in a form that is easy to use at the expense of high accuracy. The

conductivity of the solvent in equilibrium with atmospheric CO_2 is included, which causes a

somewhat higher uncertainty. The low conductivity standards are intended for water quality

control. To avoid the problem of the variation of CO_2 content, 30 % n-propanol 70 % water mixed

solvent is used in which the CO_2 effect is minimal.

Conductivity measurement is one of the most precise, accurate, and relatively inexpensive

methods for determining the ionic properties of electrolyte solutions. To ascertain the accuracy of a

measurement, a calibrated cell must be used. When calibrating cells, several standards, such as

SRMs, should be measured to validate the calibration. If the cell constants from several

measurements agree to within the measurement uncertainty, then one can be sure that the results are

accurate. If the results do not agree, the source of errors must be found and eliminated before any further measurements are made.

7. References

1. F. Kohlrausch and W. A. Nippoldt, Gott. Nach. **415** (1868).

2. F. Kohlrausch and W. A. Nippoldt, W.A., Ann. Physik **138**, 280, 370 (1869).

3. F. Kohlrausch, L. Holborn, and H. Dieselhorst, Weid. Ann. **64**, 625 (1898).

4. G. Jones and B. C. Bradshaw, J. Am. Chem. Soc. **55**, 1780 (1933).

5. Y. C. Wu, W. F. Koch, W. J. Hamer, and R. L. Kay, J. Solution Chem. **16**, 985 (1987); **19**, 1053 (1990).

6. Y. C. Wu, K. W. Pratt, and W. F. Koch, J. Solution Chem. **18**, 515 (1989).

7. R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, 3rd ed., Butterworths, London (1959).

8. Y. C. Wu, W. F. Koch, D. Feng, L. A. Holland, E. Juhasz, E. Arvay, and A. Tomek, J. Res. Natl. Inst. Stand. Technol. **99**, 241 (1994).

9. Y. C. Wu and P. Berezansky, J. Res. Natl. Inst. Stand. Technol. **100**, 521 (1995).

10. Y. C. Wu, W. F. Koch, and K. W. Pratt, J. Res. Natl. Inst. Stand. Technol. **96**, 191 (1991).

11. Y. C. Wu and W. F. Koch, J. Solution Chem. **20**, 391 (1991).

12. K. W. Pratt, W. F. Koch, Y. C. Wu, and P. A. Berezansky, *submitted for publication*

13. IUPAC Commission on Physicochemical Measurements and Standards, Pure and Appl. Chem. **53**, 1841 (1981).

14. G. Jones and R. C. Josephs, J. Am. Chem. Soc. **50**, 1049 (1928).

15. P. H. Dike, Rev. Sci. Instruments. **2**, 379 (1931).

16 H. W. Lamson, Rev. Sci. Instruments. **9**, 272 (1938).

17. H. C. Parker and E. W. Parker, J. Am. Chem. Soc. **46**, 312 (1924).

18. Y. C. Wu, W. F. Koch, and G. Marinenko, J. Res. Natl. Bur. Stand. **89**, 395 (1984); Y. C. Wu, W. F. Koch, and R. A. Durst, NBS Special Publ. 260-53 (1988).

19. *Guide to the Expression of Uncertainty in Measurement*, ISBN 92-67-10188-9, 1st Ed., International Organization for Standardization, Geneva, Switzerland, 1993.

20. L. Onsager and R. M. Fuoss, J. Phys. Chem. **36**, 2689 (1932).

21. Y. C. Wu, W. F. Koch, P. A. Berezansky, and L. A. Holland, J. Solution Chem. **21**, 383 (1992).

22. R. Sams, *private communication.*

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